MOLECULAR ASSOCIATION AS STUDIED BY RAMAN EFFECT*

By P. KOTESWARAM**

(*Received for publication, July 2, 1940*)

ABSTRACT. From a study of molecular association between similar and dissimilar molecules in a number of liquids and their mixtures, certain general conclusions are drawn as to the cause of molecular association. It has been found that, for association between two molecules, one must have a donor atom and the other an acceptor. Mere polar nature of a molecule does not facilitate association. The extent of depolymerisation of liquids on mixing is also investigated.

INTRODUCTION

Since very early times, different methods were employed for the study of molecular association in substances. Physico-chemical data based upon the elevation of boiling points and the depression of freezing points, or on the determination of surface tension and other physical constants, are subject to limitations peculiar to the constants determined and hence association factors based upon these determinations were all approximate Another relevant factor to be considered is that it is the abnormality in obeying some empirical rule which is found to hold good in a number of substances, that indicates that their molecules are associated and which gives an idea of the degree of association. These methods can in general be described as statistical, depending upon the behaviour of the substance in bulk.

With the development of newer physical methods like the determination of dielectric constants and dipole moments, X-ray and electron diffraction methods, and infra-red investigations, a direct approach is made to the molecule with a view to study its behaviour. The advent of Raman effect takes us direct to the molecule as the spectral lines recorded are due to the vibrations of individual molecules. Thus the effect of environment on the vibrations of the molecules manifests itself by producing changes in the frequencies and intensities of these lines. It is this factor that is most helpful in the study of molecular association by this method. With the presence of another molecule attached by a weak valency bond to one of its constituent atoms, the vibrations of every molecule are bound to be affected and the effects revealed as shifts

* Adapted from the thesis approved for the D.Sc. degree of the Madras University.

** Communicated by the Indian Physical Society.

in the Raman lines. What happens in every individual molecule is more or less visualised in the Raman spectra and, thus, this method gives us a direct evidence about the existence or otherwise of association. To distinguish this method from other physico-chemical methods, one relevant example may be given. In a non-polar solvent, the molecular weight of an associated solute depends upon its concentration to a certain extent. This is not due to any breaking up of the associated molecules in the solvents at low concentrations, but to other influences the nature of which is still uncertain. No such anomaly is presented in Raman spectra, the spectral lines undergoing no change with concentration of the associated substance in non-polar solvents.

One of the limitations of this method is that it may not be possible to determine the actual degree of association in a substance at a particular concentration, but by a comparison of the intensities of individual components attributed to various polymers, an attempt can be made to determine their percentage in a liquid. Typical examples are the work of Ramakrishna Rao in water,[1] in which he evaluated the relative proportions of the three types of polymers at different temperatures in water and the work of Ramakrishna Rao and the author [2] in heavy water. But even here, a determination of the absolute percentages cannot be made, only an estimate of the relative proportions at the different states being possible.

The work of the author in this field can be divided into two parts: 1. Association between similar molecules and 2. Association between dissimilar molecules.

(1) *Association between similar molecules*

The behaviour of water at different temperatures is the starting point for these investigations. Ramakrishna Rao's[1] work on its Raman band and his observations that it consists of three distinct maxima attributable to H_2O, $(H_2O)_2$, $(H_2O)_3$ molecules respectively and his determinations of the relative proportions of the different polymers at different temperatures by a comparison of the intensities of the three components of the band led to the natural extension of the work to heavy water.[2] Heavy water also is found to give rise to a broad Raman band with three distinct maxima at 2394, 2534, and 2674 cm^{-1}. With increasing temperature, as in the case of ordinary water, the band is found to undergo structural variations indicating a decrease in the intensity of the low frequency component 2394 and a corresponding increase in intensity of the high-frequency component 2674, the middle component 2534 remaining more or less unchanged in intensity. The third component 2674 being very close to the frequency of the heavy water vapour line, is naturally attributed to single D_2O molecules and the other two components to $(D_2O)_2$ and $(D_2O)_3$ molecules for reasons analogous to those for ordinary water. The decrease in the intensity of the low-frequency component at 2304 with increasing

temperature is explained as due to the decrease in the proportion of the $(D_2O)_3$ molecules and the increase in the intensity of the high-frequency component is attributed to the corresponding increase in the proportion of the D_2O molecules.

The fatty acids were studied next by the same method, the substances selected being acetic,[3] formic and benzoic acids.[4] The C=O oscillation in these compounds is found to undergo conspicuous changes under different conditions. The effect of increased temperature on the three acids studied is to shift the maximum of the C=O frequency towards higher values. This result which is analogous to that in water and heavy water is explained as due to the breaking up of the associated molecules in the fatty acids into simpler ones. Dilution in water also produces distinct shifts of the C=O band towards higher frequencies, an effect which is attributed to the breaking up of the associated fatty acid molecules into simpler ones. The effect on methyl alcohol in aqueous solutions is dissimilar to that of acetic acid, the C=O line of the alcohol shifting to shorter frequencies unlike the C=O line of the acid. No definite conclusions can be arrived at in the case of methyl alcohol till a study of the OH band of the alcohol is made in a number of associating solvents.

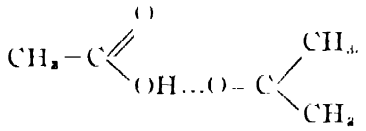
(2) *Association between dissimilar molecules*

The molecules of the liquids described in the previous section are all associated among themselves and seem to break up at higher temperatures and at higher dilutions in polar solvents like water. There is another type of liquids which are normal by themselves, but which have a strong tendency to associate with other suitable molecules. Thus there is the possibility of association being produced between the solvent and the solute.

The effect of a number of solvents on acetone[5] was studied with a view to detect any association between acetone molecules and those of the solvent. The C=O line of acetone is the one observed to undergo conspicuous changes. In addition, the C–C line is also affected. Non-polar solvents like benzene and carbon-tetrachloride and polar normal solvents like ether and chloroform do not produce any effect on the acetone lines. Water, methyl alcohol, phenol and acetic acid produce shifts in the C=O line towards smaller frequencies and in the C–C line towards larger frequencies. A number of deformation oscillations are also shifted towards higher frequencies. Similar results are obtained in the case of methyl-ethyl ketone. These results are explained as due to the formation of complexes between the ketone and the other component in the solution studied, *viz.*, water, methyl alcohol, phenol, and acetic acid.

The Raman spectra of mixtures of acetic acid and acetone[6] and also of acetic acid and methyl-ethyl ketone[7] contain a new line at 1760, not present

either in the pure ketone or in the pure acid. Moreover, the C–C line of the ketone shifts to longer frequencies as in the case of mixtures of the ketone with water and phenol while the C–C line of the acid at 898 doubles up at higher dilutions, its low-frequency component at 872 increasing in intensity with a corresponding decrease in the intensity of the line 898. This significant change is also observed in solutions of acetic acid in ether. But nitrobenzene does not produce a change in the C–C line but as in the case of solutions of acetic acid in acetone, methyl-ethyl ketone and ether, solutions in nitrobenzene reveal the new line at 1760. Chloroform does not produce any conspicuous shifts and non-polar solvents like benzene and carbon-tetrachloride do not produce any effect on the acetic acid lines. The changes observed in the Raman frequencies of acetic acid in solutions in ketones and in ether are explained by the formation of complexes of the type



by the hydrogen bonding between the O of the ketone and the H of the OH in the acid. The 1760-line is attributed to the externally unattached C=O in the acid molecule in the complex. The low-frequency components of the 893- and the 620-lines which are feeble in the pure acid are pointed out as lending additional support to the concept of the association between acetic acid and the ketone or ether. In nitrobenzene, the absence of these components and the presence of the 1760-line is explained on the assumption that the associated molecules in the pure acid are merely broken up in solution, unaccompanied by association with molecules of nitrobenzene.

Acetic acid is thus found exhibiting two different properties. It does not seem to hydrate with water, the effect seeming to be merely towards a breaking up of the higher polymers into lower ones, whereas in acetone, methyl ethyl ketone and in ether it seems to combine with them to form complexes. Reasons for supposing that it does not hydrate with water are: the high-frequency shift of the C=O line, the absence of the 1760-line characteristic of the complexes and the absence of the low-frequency components of the 620- and the 898-lines also characteristic of the complexes, in aqueous solutions.

CONCLUSIONS

The foregoing work leads to the following generalisations with regard to molecular association in liquid.

(1) The mere polar nature of molecule does not give it associating properties, *e.g.*, chloroform and nitrobenzene.

(2) The substance must have both a donor and an acceptor atom for association in the pure state, *e.g.*, water and fatty acids.

(3) Molecules having only a donor or an acceptor atom cannot associate with those of the same type, *e.g.*, acetone. But they can form complexes with those having an acceptor or a donor atom, *e.g.*, acetone + water, acetone + phenol, acetone + acetic acid, etc.

(4) Non-polar liquids do not have any effect on polar solvents either normal or associated, *e.g.*, benzene + acetone, benzene + acetic acid.

(5) Polar normal liquids not having a donor or an acceptor atom do not have any effect on other polar liquids whether they have a donor or an acceptor, *e.g.*, chloroform + acetone, ether + acetone.

(6) Normal polar liquids which have a high dipole moment seem to split up associated liquids without combining with them to form complexes, *e.g.*, nitrobenzene + acetic acid.

(7) Two associated liquids seem to have mutual splitting effect on each other, there being no evidence for cross-association. These conclusions confirm the results from other physico-chemical methods.

The author's thanks are due to Dr. Ramakrishna Rao under whose guidance the work was done and to the authorities of the Andhra University for the facilities given.

REFERENCES

1 *Proc. Roy. Soc., A*, **130**, 498 (1931).
2 *Ind. Jour. Phys*, **12**, 63 (1938).
3 *Zeits f. Physik.*, **110**, 118 (1938).
4 „ „ **112**, 395 (1939).
5 *loc. cit.*
6 *Current Science*, **8**, 70 (1939).
7 *loc cit.*